Quantum-classical correspondence in the hydrogen atom in weak external fields

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The complex processes leading to the collisional population of ultralong-lived Rydberg states with very high angular momentum can be explained surprisingly well using classical mechanics. In this article, we explain the reason behind this striking agreement between classical theory and experiment by showing that the classical and quantum dynamics of Rydberg electrons in weak, slowly varying external fields agree beyond the mandates of Ehrenfest's Theorem. In particular, we show that the expectation values of angular momentum and Runge-Lenz vectors in hydrogenic eigenstates obey exactly the same perturbative equations of motion as the time averages of the corresponding classical variables. By time averaging the quantum dynamics over a Kepler period, we extend this special quantum-classical equivalence to Rydberg wave packets relatively well localized in energy. Finally, the perturbative equations hold well also for external fields beyond the Inglis-Teller limit, and in the case of elliptic states, which yield the appropriate quasiclassical initial conditions, the matching with classical mechanics is complete.

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I. INTRODUCTION

In the past few years new experimental techniques have made possible the study of the dynamics of atoms or molecules in which an electron is promoted to a very high energy state, where it is only weakly bound to the core [1]. These high energy states can be described by approximately hydrogenic wave functions with very large principal quantum numbers ($n \gtrsim 100$) [2, 3]. The atoms (or molecules) in which a valence electron is promoted to such high-n states are generically called "Rydberg" atoms, because the energy levels of the excited electron are well described by a Rydberg-like formula [2], and their highly energetic electron is known as a Rydberg electron. In such systems the weakly bound Rydberg electron resides mostly at an immense distance from the atomic core, a distance so large that if Rydberg atoms were solid, they would be just about visible to the naked eye. Laboratory-scale external fields, and even weak stray electric fields [4–8], become then comparable to the atomic Coulomb field sensed by the Rydberg electron, so that the dynamics of the electron can be probed with accuracy, and also fundamental dynamical properties such as quantum manifestations of chaos [9–14], can be studied experimentally.

To a very good approximation, the dynamics of Rydberg electrons is hydrogenic. More precisely, small deviations from the purely hydrogenic eigenenergies are introduced by the interaction between the far flung electron and the electronic cloud around the atomic or molecular core. These deviations are quantified by the quantum defect δ_ℓ, which enters in the formula for the energy levels as a correction to the principal quantum number n [2, 15]. However, the quantum defect becomes rapidly negligible as the angular momentum of the electron increases. In fact, more complex atoms are often used as experimental substitutes for hydrogen, since it is much easier to excite their valence electron to a Rydberg state, and yet the field sensed by the Rydberg electron does not differ much from a pure Coulomb field. Therefore many recent investigations of Rydberg electrons in alkali atoms have really probed the dynamics of quasiclassical electrons in an essentially coulombic potential. These accurate experimental results have led to a renewed theoretical interest in the hydrogen atom in external fields in the limit of large quantum numbers, [10, 16–19] which has become one of the paradigmatic models for the study of quantum chaos [9–14], and of quantum-classical correspondence in general.

Since the degeneracy of a hydrogenic n-manifold grows as n^2, a fully quantum treatment of the dynamics of Rydberg electrons poses formidable challenges even to the most advanced computers. Therefore classical mechanics is often the only practical way to study such systems, under the assumption that for large n's classical and quantum predictions should somehow converge. Interestingly, however, recent experimental and theoretical work on electronic wave packets in hydrogenic systems [20–45] have shown very clearly that the quantum mechanical properties of the Rydberg electron are essential to the dynamics of the wave packet, even in the large-n regime. For example, the observation of fractional revivals can be explained only by the quantized spectrum of the Hamiltonian [20–22, 25, 27–29] in spite of the very large principal quantum numbers involved, which seems to suggest that large quantum numbers are not sufficient to ensure the accuracy of a purely classical description of Rydberg dynamics.

On the other hand, classical mechanics yields surprisingly accurate results for the problem of the hydrogen atom in weak, slowly varying external fields; i.e., when

the classical electron still moves, to a good approximation, along a Kepler ellipse, and the semimajor axis of the ellipse (or, equivalently, the Kepler energy of the electron) remains unchanged. In particular, recent classical, perturbative calculations [4, 46–51] have succeeded in explaining several diverse experimental results with astonishing accuracy, ranging, for example, from the ultralong lifetimes of the molecular high-n states employed in zero-electron-kinetic-energy (ZEKE) spectroscopy [5–7, 47, 48, 52–58], to the intrashell transitions induced in alkali Rydberg atoms by slow ion-Rydberg collisions [47, 48, 59–63]. The same classical approach also explains the anomalous autoionization lifetimes of Rydberg electrons in circularly polarized microwave fields [49, 64] and the dynamics and stability of circular Rydberg states (i.e., states with maximum angular momentum) in weak, slowly rotating electric fields [4, 50]. Clearly, the success of the classical treatment must stem from some special equivalence between classical and quantum predictions in the hydrogen atom in weak external fields: in fact, such equivalence has been already simply observed (but not explained) only in the limited case of states with initial zero angular momentum [65, 66].

In this work we show that the accuracy of the classical results does indeed rest on a particularly direct connection between classical and quantum predictions, and demonstrate explicitly that in the perturbative limit the quantum expectation values of the angular momentum and the Runge-Lenz vector obey *exactly the same equations as the time averaged classical variables*. We also investigate the conditions on the fields for which the perturbative approach holds, and we find that classical mechanics seems to require more relaxed constraints on the external fields than quantum mechanics, as the classical condition for the conservation of the Kepler energy -see below- is not equivalent to the quantum condition for negligible intermanifold mixing. However, by studying in detail the contributions to the dynamics which stem from n-mixing, we demonstrate that the perturbative equations of motion for the quantum expectation values remain accurate also under the less restrictive classical conditions, as long as the dynamics is time averaged over a Kepler period. In fact, the time averaged equations describe well the dynamics of quantum expectation values also when the Rydberg electron is initially excited in a superposition of hydrogenic n-manifolds, i.e., its initial state is not a stationary eigenstate of the unperturbed Hamiltonian, but a time dependent wave packet. Interestingly, time averaging is precisely the same procedure which leads to the classical perturbative equations, and therefore our result is an explicit example of how the scrambling of the principal quantum number (quantum decoherence) brings about a more direct quantum-classical correspondence. Finally, we show that for special superpositions of the eigenstates of the bare Hamiltonian (that is, elliptic states [29, 67, 68]) and in the limit of large principal quantum numbers, the quantum expectation values also have the appropriate quasiclassical initial conditions. Most importantly, elliptic states are not merely theoretical constructs: they have been prepared in the laboratory and some of their properties have already been studied experimentally [8, 69–71].

Our findings are not merely an application of Ehrenfest's theorem [72]. Although Ehrenfest's theorem relates the time evolution of the quantum expectation values to the classical equations of motion, it does not state that quantum expectation values and classical variables obey *exactly* the same equations. Such an identity holds only for the harmonic oscillator and, albeit trivially, also for the free particle and any linear potential. Because the harmonic oscillator is often used as a textbook example, it often leads to the incorrect impression that such exact equivalence is of more general nature. In truth this correspondence is a very special property of potentials which are at most quadratic, because in general the expectation value of the "force operator" $f(\hat{\mathbf{r}}) = -\nabla V(\hat{\mathbf{r}})$, which is a function of quantum observables, is not equal to the same function evaluated at the expectation values of the observables; that is (in general):

$$\langle\psi|f(\hat{\mathbf{r}})|\psi\rangle \neq f(\langle\psi|\hat{\mathbf{r}}|\psi\rangle) \; . \tag{1}$$

In the very special case of the harmonic oscillator, for example, the restoring force of the spring is simply proportional to $\hat{x}$ and the two sides of Eq. (1) are identical, hence the exact correspondence between quantum and classical evolution. Also, the perturbative treatment of the Kepler problem borrows heavily from the methods of celestial mechanics [73] and studies the dynamics of time averages of the classical variables. Such an approach is not the same as an expansion of the Hamiltonian around an equilibrium point and up to quadratic terms in the potential, which would make the system trivially equivalent to a harmonic oscillator. Therefore, our work amounts to an extension of Ehrenfest theorem, in a much stronger form, for the important case of the hydrogen atom in weak, slowly varying external fields.

This paper is organized as follows: in section II we derive explicitly the equations of motion for the quantum expectation values over states confined within a hydrogenic n-manifold, and show that they coincide with the classical perturbative equations to first order in the fields. In section III we investigate the contributions to the dynamics due to the intermanifold mixing: we show that the same perturbative equations of motion remain accurate even if the state is not initially confined within a specific n-manifold, as long as one considers the time average (over a Kepler period) of the dynamics. In section IV we study the initial conditions for the quantum expectation values over different quantum states and also discuss a few physical implications of our results. Finally in section V we draw some general conclusions.

II. CLASSICAL AND QUANTUM EQUATIONS

In atomic units (which we use throughout this paper) the Hamiltonian for a hydrogen atom in crossed electric and magnetic field is:

$$H = \frac{p^2}{2} - \frac{1}{r} - \omega_L L_z + Fx + \frac{\omega_L^2}{2}(x^2 + y^2) \,, \qquad (2)$$

where the electric field is parallel to the x-axis and its strength is F; the magnetic field is antiparallel to the z-axis and ω_L is the Larmor frequency of the magnetic field, which in atomic units is equal to half the strength of the field. For weak fields the diamagnetic term, which is proportional to the square of the field, can be neglected, and the Hamiltonian becomes identical to the one for a hydrogen atom in a weak electric field rotating with frequency ω_L, in the noninertial frame which rotates with the field [17, 47–50].

The classical perturbative treatment of the hydrogen atom in weak, external fields is based on the methods of celestial mechanics, and one is interested in the secular variation of the elements of the Kepler ellipse followed by the classical electron [73]. While a Kepler ellipse can be described by many equivalent sets of elements, the equations of motion are particularly simple if one chooses the angular momentum and the Runge-Lenz vector. Therefore, the dynamical variables of the classical problem are the time averages over a Kepler period, and along a Kepler ellipse (which is the classical solution to zeroth order in the external fields), of the angular momentum $\mathbf{L}$ of the electron, and its scaled Runge-Lenz vector $\mathbf{a}$, which for bound states is defined as [74]:

$$\mathbf{a} = \frac{1}{\sqrt{-2E}} \left\{ \frac{1}{2} \left(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p} \right) - \frac{\mathbf{r}}{r} \right\} \,, \qquad (3)$$

where $E = -1/2n^2$ is the Kepler energy of the electron. The antisymmetrization of the cross product is not necessary in classical mechanics, but is essential in quantum mechanics to obtain a hermitian operator [75, 76]. To first order in the external fields the classical, time averaged angular momentum and scaled Runge-Lenz vector (which for the sake of a simpler notation we will still indicate respectively as $\mathbf{L}$ and $\mathbf{a}$) satisfy the following equations of motion [47, 77–80]:

$$\begin{aligned} \frac{d\mathbf{L}}{dt} &= -\boldsymbol{\omega}_S \times \mathbf{a} + \boldsymbol{\omega}_L \times \mathbf{L} \\ \frac{d\mathbf{a}}{dt} &= -\boldsymbol{\omega}_S \times \mathbf{L} + \boldsymbol{\omega}_L \times \mathbf{a} \,, \end{aligned} \qquad (4)$$

where $\boldsymbol{\omega}_S$ is the Stark frequency of the electric field, and is defined as:

$$\boldsymbol{\omega}_S = \frac{3}{2} n \mathbf{F} \,, \qquad (5)$$

and $\boldsymbol{\omega}_L$ is the Larmor frequency vector: it is directed along the external magnetic field and its magnitude is equal to the Larmor frequency of the field itself.

Eqs. (4) were derived originally by Born [77] and in classical mechanics they remain accurate as long as the two frequencies (Stark and Larmor) are much smaller than the Kepler frequency ω_K of the electron [47, 77–80]:

$$\omega_S \,, \, \omega_L \ll \omega_K = \frac{1}{n^3} \,. \qquad (6)$$

In classical mechanics Eq. (6) means that the elements of the Kepler orbit do not vary significantly over a Kepler period, so that the classical electron still moves, to a good approximation, along a Kepler ellipse, and the Kepler energy of the classical electron is conserved. In fact, the classical angular momentum and the Runge-Lenz vector obey two constraint equations [74]:

$$\begin{aligned} &\mathbf{L} \cdot \mathbf{a} = 0 \\ &L^2 + a^2 = n^2 \,. \end{aligned} \qquad (7)$$

It is easy to see that both constraints are invariant under the time evolution dictated by Eqs. (4), and also that the second of Eqs. (7) implies the conservation of the Kepler energy of the electron.

Instead, the quantum mechanical interpretation is that the external fields remove the degeneracy of the n^2 unperturbed states of the hydrogenic n-manifold, and the conditions of Eq. (6) mean that the energy difference between two adjacent perturbed states is much smaller than the separation between adjacent, unperturbed Rydberg energy levels. However, this is not the usual condition under which in quantum mechanics inter-n mixing is negligible. For example, in the case of just an external d.c. field (the extension to include also a magnetic field is straightforward [81]) the energy separation between the lowest and the highest Stark states for a fixed principal quantum number n is (to first order in the field) [82]:

$$\Delta E = 3n(n-1)F \,. \qquad (8)$$

Therefore the approximate condition for level crossing of the highest Stark state from a given n-manifold with the lowest Stark level from the next n-manifold is given by the Inglis-Teller limit [2]:

$$3n^2 F \approx \frac{1}{n^3} \,. \qquad (9)$$

Clearly, in the semiclassical limit the quantum condition on the external fields for negligible n-mixing of Eq. (9) is much stronger than the classical condition of Eq. (6). We show below, however, that the perturbative treatment of the dynamics of the quantum expectation values remains accurate also in presence of some degree of n-mixing induced by the external fields, as long as the dynamics is time averaged over a Kepler period.

In this section we confine our study to the dynamics of the quantum expectation values of the angular momentum and the scaled Runge-Lenz vector operators (that is, $\langle\psi|\hat{\mathbf{L}}|\psi\rangle$ and $\langle\psi|\hat{\mathbf{a}}|\psi\rangle$; throughout this paper we use boldface letters for vectors, and a caret indicates a quantum

operator, not a unit vector which we denote instead as $\mathbf{e}_\imath$) over superpositions of the hydrogen atom eigenfunctions with a well defined principal quantum number; i.e., over states $|\psi_n\rangle$ which are localized within a hydrogenic n-manifold. More precisely, we show here that to first order in the external fields the quantum expectation values obey exactly the same equations of motion as Eqs. (4).

The cornerstone of the study of hydrogenic systems in weak, external fields is the so-called Pauli's repacement [75, 76], according to which the matrix elements *between states within the same n-manifold* of the position operator are directly proportional to the corresponding matrix elements of the Runge-Lenz vector operator:

$$\langle n\ell' m'|\hat{r}_\imath|n\ell m\rangle = -\frac{3}{2}n\langle n\ell' m'|\hat{a}_\imath|n\ell m\rangle \ . \tag{10}$$

By replacing the position operator, which appears in the perturbation Hamiltonian for an external field, with $-3n\hat{\mathbf{a}}/2$ the demonstration of quantum-classical equivalence *within an n-manifold* is straightforward [31, 51, 83], but nothing can be said about the intermanifold dynamics. Instead, in our argument we do not apply Pauli's replacement directly in the Hamiltonian; our approach is more complicated, but it makes possible the extension of our analysis (in the next section) also to the dynamics of Rydberg wave packets. Moreover, we will be able to show that the quantum analogs of Eqs. (4) remain accurate under the more relaxed, classical conditions on the external fields given in Eq. (6).

To prove the special quantum-classical equivalence, we will make use of the following identity, which holds within a hydrogenic manifold and which we derive explicitly in Appendix A:

$$\langle\psi_n|\hat{r}_\imath\hat{p}_\jmath|\psi_n\rangle = -\langle\psi_n|\hat{p}_\imath\hat{r}_\jmath|\psi_n\rangle \ , \tag{11}$$

where $\hat{r}_\imath$ and $\hat{p}_\jmath$ are components of the position and momentum operator respectively.

Indeed, armed with the result of Eq. 11 it is easy to show that to first order in the external fields the expectation values of the quantum observables satisfy the same equations as the time averages (over a Kepler period) of the classical variables.

The equations of motion of the quantum expectation values are straightforward in the Heisenberg picture [72]:

$$\begin{aligned}\langle\psi_n|\frac{d\hat{L}_\imath}{dt}|\psi_n\rangle &= -i\langle\psi_n|\left[\hat{L}_\imath,\hat{H}\right]|\psi_n\rangle \\ \langle\psi_n|\frac{d\hat{a}_\imath}{dt}|\psi_n\rangle &= -i\langle\psi_n|\left[\hat{a}_\imath,\hat{H}\right]|\psi_n\rangle \ .\end{aligned} \tag{12}$$

and we now show that they are identical to Eqs. (4).

The classical equations (4) contain two terms, an electric term which is proportional to the Stark frequency ω_S, and which couples the angular momentum to the scaled Runge-Lenz vector; and a magnetic term which is proportional to the Larmor frequency ω_L of the field (or to the rotation frequency of a slowly rotating electric field, in a noninertial frame rotating with the field itself [17, 47–50]). Both the scaled Runge-Lenz vector and the angular momentum commute with the hydrogenic Hamiltonian (they are invariants of the pure Kepler problem) [74]. Moreover, it is easy to see that the magnetic term of the classical equations can be recovered by invoking the vectorial properties of $\hat{\mathbf{a}}$ and $\hat{\mathbf{L}}$, because of which their commutators with the magnetic term in of the Hamiltonian (i.e., $-\omega_L\hat{L}_z$) obey the well known rule [72]:

$$\left[\hat{V}_\imath,\hat{L}_\jmath\right] = i\epsilon_{\imath,\jmath,k}\hat{V}_k \ , \tag{13}$$

where $\hat{V}_\imath$ stands for the $\imath^{th}$ component of any vector operator.

Therefore, we only need to investigate the commutators of $\hat{\mathbf{a}}$ and $\hat{\mathbf{L}}$ with the electric perturbation $F\hat{x}$.

We begin with $\hat{a}_y$:

$$\begin{aligned}-iF\left[\hat{a}_y,\hat{x}\right] &= -i\frac{n}{2}F\left\{\left[\left(\hat{p}_z\hat{L}_x-\hat{p}_x\hat{L}_z\right),\hat{x}\right]\right. \\ &\left.-\left[\left(\hat{L}_z\hat{p}_x-\hat{L}_x\hat{p}_z\right),\hat{x}\right]\right\} = -i\frac{n}{2}F\Big\{-\hat{p}_x\left[\hat{L}_z,\hat{x}\right] \\ &-\left[\hat{p}_x,\hat{x}\right]\hat{L}_z-\hat{L}_z\left[\hat{p}_x,\hat{x}\right]-\left[\hat{L}_z,\hat{x}\right]\hat{p}_x\Big\} \\ &= nF\left\{\hat{L}_z-\hat{y}\hat{p}_x\right\} \ .\end{aligned} \tag{14}$$

However, using the identity of Eq. (11) one has:

$$-\langle\psi_n|\hat{y}\hat{p}_x|\psi_n\rangle = \frac{1}{2}\langle\psi_n|\hat{x}\hat{p}_y-\hat{y}\hat{p}_x|\psi_n\rangle \ , \tag{15}$$

from which it follows:

$$-iF\langle\psi_n|\left[\hat{a}_y,\hat{x}\right]|\psi_n\rangle = \frac{3}{2}nF\langle\psi_n|\hat{L}_z|\psi_n\rangle \ . \tag{16}$$

This is the same as the electric term in the equation of motion for the classical time averaged a_y.

The derivation of the electric term for the equation of of $\langle\psi_n|\hat{a}_z|\psi_n\rangle$ follows along the same lines and it is easy to see that it yields the desired result.

We then consider $\hat{a}_x$:

$$\begin{aligned}-iF\left[\hat{a}_x,\hat{x}\right] &= \frac{n}{2}F\left\{\left[\left(\hat{p}_y\hat{L}_z-\hat{p}_z\hat{L}_y\right),\hat{x}\right]\right. \\ &\left.-\left[\left(\hat{L}_y\hat{p}_z-\hat{L}_z\hat{p}_y\right),\hat{x}\right]\right\} = -i\frac{n}{2}F\Big\{\hat{p}_y\left[\hat{L}_z,\hat{x}\right] \\ &-\hat{p}_z\left[\hat{L}_y,\hat{x}\right]-\left[\hat{L}_y,\hat{x}\right]\hat{p}_z+\left[\hat{L}_z,\hat{x}\right]\hat{p}_y\Big\} \\ &= \frac{n}{2}F\left\{\hat{p}_y\hat{y}+\hat{y}\hat{p}_y+\hat{p}_z\hat{z}+\hat{z}\hat{p}_z\right\} \ .\end{aligned} \tag{17}$$

Invoking once again Eq. (11) one obtains immediately:

$$F\langle\psi_n|\left[\hat{a}_x,\hat{x}\right]|\psi_n\rangle = 0 \ , \tag{18}$$

which is the same as the right hand side of the corresponding classical equation of motion.

Finally, we turn to the equations for the angular momentum. The classical equations can be written as:

$$\frac{dL_\imath}{dt} = -\epsilon_{\imath,j,k}\omega_{Sj}a_k = -\frac{3}{2}nF\epsilon_{\imath,1,k}a_k \ , \qquad (19)$$

where we have specialized the right hand side to the case of an external field along the x-axis. Using once again the vector properties of $\hat{\mathbf{r}}$, the contribution of the electric term to the quantum equations is:

$$-iF\left[\hat{L}_\imath, \hat{x}\right] = F\epsilon_{\imath,1,k}\hat{r}_k \ . \qquad (20)$$

This is not yet in the desired form. However, within a given n-manifold one can apply Pauli's replacement [75, 76] according to which:

$$\langle n\ell' m'|\hat{r}_\imath|n\ell m\rangle = -\frac{3}{2}n\langle n\ell' m'|\hat{a}_\imath|n\ell m\rangle \ . \qquad (21)$$

Pauli's replacement is mathematically exact, and yet physically it is just an approxximation, because the dynamics of the electron is only approximately confined within a given n-manifold. Clearly, the accuracy of the approximation rests on certain conditions on the external fields, depending on which the dynamics may -or may not- be very well localized within a hydrogenic manifold, and we discuss such conditions in detail below. However, in the present section we are interested only the intramanifold dynamics, and therefore one has:

$$F\epsilon_{\imath,1,k}\langle\psi_n|\hat{r}_k|\psi_n\rangle = -\frac{3}{2}nF\epsilon_{\imath,1,k}\langle\psi_n|\hat{a}_k|\psi_n\rangle \ , \qquad (22)$$

which is the same electric term as in the right hand side of the corresponding classical equations of motion, and our proof is complete.

Our derivation of the equations of motion of the quantum expectation values is accurate only to first order in the fields because it relies heavily on the identity of Eq. (11), which holds for the unperturbed $|\psi_n\rangle$ states; these are eigenstates of the hydrogen atom Hamiltonian and therefore are *quantum solutions to zeroth order in the fields*. In fact, this is exactly in the same spirit as the classical approach, where the right hand sides of Hamilton equations are time averaged over a Kepler period and, most importantly, along Kepler ellipses, which are the *classical solutions to zeroth order in the fields*.

The same consideration can also be cast in the language of operators, by observing that we have proven Eq. (11) only for the time independent operators of the Schrödinger picture, whereas in the right hand side of the equations of motion one must more correctly use the time dependent operators of the Heisenberg picture. However, in a first order approximation one may assume that the time evolution of the operators in the Heisenberg picture is dictated solely by the hydrogenic propagator, which commutes with both $\hat{\mathbf{L}}$ and $\hat{\mathbf{a}}$, so that one can legitimately use the properties of those operators in the Schrödinger picture.

Since Eq. (11) holds for all possible pairs of indexes $\{j, k\}$, the same derivation can be easily extended to the case of slowly varying (both in magnitude and direction) electric and magnetic fields, in which case the perturbing Hamiltonian $\hat{H}_1$ becomes:

$$\hat{H}_1 = \sum_\imath \left\{F_\imath(t)\hat{r}_\imath - \omega_{L_\imath}(t)\hat{L}_\imath\right\} \ . \qquad (23)$$

However, the most important feature of our proof is that we have not applied Pauli's replacement directly in the Hamiltonian [31, 51, 83]. An early application of Pauli's replacement yields a straightforward proof of quantum-classical equivalence *within an n-manifold*, but it erases all information about the precise conditions on the fields under which the perturbative classical equations of motion constitute an accurate description of the dynamics of the quantum expectation values. Moreover, it also makes impossible to study the corrections to the dynamics due to intermanifold mixing and therefore one could not extend Eqs. (4) to the case of Rydberg wave packets. Instead, in the next section we address in detail precisely these important issues.

III. INTERMANIFOLD DYNAMICS AND QUANTUM-CLASSICAL CORRESPONDENCE IN RYDBERG WAVE PACKETS

In this section we study intermanifold mixing and the conditions on the external fields under which the classical perturbative equations of motion offer an accurate treatment of the dynamics of the quantum expectation values. We will show that the same conditions as in classical mechanics hold in quantum mechanics too, provided that the dynamics is time averaged over a Kepler period. Most importantly, we will demonstrate that upon time averaging Eqs. (4) apply also to the case of Rydberg wave packets.

For the sake of simplicity we restrict our analysis to the pure Stark case, that is when there is no external magnetic field; the extension to the more general case including a weak magnetic field is straightforward. Therefore, in this section we assume a simplified Hamiltonian:

$$\hat{H} = \hat{H}_0 + F\hat{x} \ , \qquad (24)$$

where $\hat{H}_0$ is the hydrogen atom Hamiltonian and F is again the strength of the external electric field.

Inter-manifold mixing is due to two main causes, depending on how the Rydberg state is prepared. If the Rydberg electron is initially confined within a hydrogenic n-manifold, then n-mixing is induced by the applied external field, and in that case the intermanifold contributions to the equations of motion are of second order in the applied field. Note that this is a very realistic picture for slow ion-Rydberg collisions [47, 48, 59–63]. In

fact, ion-Rydberg collisions are actually gentle encounters at very large ion-Rydberg separation, which are effective because of the long-range nature of the coulomb interaction, and are very accurately modeled by a time dependent, weak external field acting on the Rydberg electron [47, 48]. Typically, the Rydberg state is prepared in absence of external dc fields, and the weak field of the colliding ion is turned on adiabatically as the ion slowly approaches the Rydberg atom. In such situation, the analysis of intermanifold mixing is equivalent to the study of the second order corrections to the equations of motion, and it allows one to determine for what precise conditions on the external electric field such corrections are negligible.

However, n-mixing can also be present at the outset, either if the Rydberg state is prepared in presence of the applied dc field and the field is strong enough to mix adjacent Rydberg levels, or alternatively if a short, large bandwidth laser pulse is employed in the preparation of the Rydberg state. In both cases the ground state is coupled to a *distribution* of hydrogenic manifolds, and the Rydberg electron is not excited to a high energy, stationary eigenstate of the hydrogen atom, but rather to some time dependent wave packet. To a first approximation the Rydberg wave packet oscillates with the Kepler frequency of the eigenstate around which the distribution of principal quantum numbers is centered; therefore a Rydberg wave packet contributes rapidly oscillating, intermanifold terms to the equations of motion for the quantum expectation values. Such intermanifold contributions may be of first order in the external field. In this section we extend the validity of the classical, perturbative Eqs. (4) precisely to the case of Rydberg wave packets, by time averaging the equations of motion over a Kepler period and by showing that the *secular*, intermanifold contributions to the dynamics remain negligible under the classical conditions of Eq. (6) for the external field.

More precisely, the wave function of a Rydberg wave packet is:

$$|\psi(t)\rangle = \sum_n C_n |\psi_n(t)\rangle \ , \tag{25}$$

and the Heisenberg equations of motion for the expectation values of either $\hat{\mathbf{L}}$ or $\hat{\mathbf{a}}$ over the state of Eq. (25) include "off-diagonal" matrix elements (for the sake of brevity we call "off-diagonal" the matrix elements of any operator between states from two different hydrogenic manifolds; whereas we will call "diagonal" the matrix elements between two states within the same n-manifold, regardless of their angular momentum quantum numbers).

For example, if we indicate generically by $\hat{O}_{cl} + \hat{O}_q$ the combinations of operators in the right hand side of the Heisenberg equations of motion, in the case of $\hat{L}_\imath$ one has:

$$\frac{d}{dt}\langle\psi|\hat{L}_\imath(t)|\psi\rangle = F\Big\{ \sum_n |C_n|^2 \, \langle\psi_n|\hat{O}_{cl}(t) + \hat{O}_q(t)|\psi_n\rangle + \sum_{\substack{n',n \\ n'\neq n}} \bar{C}_{n'} C_n \langle\psi_{n'}|\hat{O}_{cl}(t) + \hat{O}_q(t)|\psi_n\rangle \Big\} \ . \tag{26}$$

where $\hat{O}_{cl}$ indicates a combination of operators which correspond to the classical variables in the right hand side of the classical equations of motion (i.e., a combination of angular momentum and Runge Lenz vector). Instead, $\hat{O}_q$ indicates the purely quantum corrections, which vanish when the motion is exactly confined within a hydrogenic manifold. Obviously, an identical expression holds also for the equation of motion of the expectation value of $\hat{a}_\imath$

The expectation values of the operators of $\hat{O}_{cl}$ appear in the equations of motion in the same way as the classical time averaged variables, and therefore they evolve in time exactly like their classical counterparts. This is true even if the state is not confined within a hydrogenic manifold. Yet, for states which are spread over more than one n-manifold the quantum contributions from the expectation value of $\hat{O}_q$ do not vanish exactly. In fact, we proved in the previous section and in Appendix A that only the diagonal matrix elements of $\hat{O}_q$ vanish, but the same does not hold for the off-diagonal matrix elements.

However, we show below that under the classical conditions for the external field, and upon time averaging, all the off-diagonal matrix elements of the double sum of Eq. (26) offer a negligible contribution to the dynamics. In our demonstration we do not distinguish between the two operators, and treat $\hat{O}_{cl} + \hat{O}_q$ as a single term which, for the sake of brevity, we simply denote as $\hat{O}$. That is, our argument demonstrates that also the off-diagonal matrix elements of $\hat{O}_{cl}$ yield only negligible contributions to the equations of motion. Therefore, the quantum dynamics of the expectation values of the operators of $\hat{O}_{cl}$ is determined only by the intramanifold terms. Note that this last observation is not essential to the issue of quantum-classical correspondence.

Before our demonstration, however, we must discuss briefly the operators of Eq. (26) and the magnitude of their matrix elements between two eigenstates of the hydrogen atom. From the previous section, and also from Appendix A, it is easy to see that the sum of the two combination of operators $\hat{O}_{cl} + \hat{O}_q = \hat{O}$ may be equal to one or a combination of the following operators:

$$\hat{O} \sim \begin{cases} \hat{r}_\imath \\ n\hat{p}_\imath \hat{r}_\jmath \quad \imath,\jmath = 1,2,3 \\ n\hat{L}_\imath \end{cases} \ , \tag{27}$$

First, the $n\hat{L}_\imath$ operator yields matrix elements the magnitudes of which are at most $\lesssim n^2$. Moreover, $\hat{L}_\imath$ commutes with the hydrogen atom Hamiltonian and therefore all its off-diagonal matrix elements vanish, and it is very easy to prove that its intermanifold contributions to the dynamics are negligible (see below).

Next, in the case of $\hat{r}_\imath$ the magnitude of the matrix elements and, most importantly, their *scaling* with n are

determined solely by the *radial* matrix elements:

$$R^{n',\ell'}_{n,\ell} = \langle n\ell m|\hat{r}|n'\ell'm'\rangle \ . \tag{28}$$

If $n' = n$ one has [82]:

$$R^{n,\ell}_{n,\ell-1} = R^{n,\ell-1}_{n,\ell} = -\frac{3}{2}n^2\sqrt{1-\frac{\ell^2}{n^2}} \ , \tag{29}$$

whereas if $n' \neq n$ the radial matrix elements of the position operator are given by a complicated formula which involves hypergeometric functions [82]. However for $n', n \gg 1$, $\left|R^{n',\ell'}_{n,\ell}\right|$ is accurately approximated by a well known semiclassical result [84]:

$$\begin{aligned}&\left|R^{n',\ell'}_{n,\ell}\right| \\ &\approx \left|\frac{n_c^2}{2\Delta_{n,n'}}\left\{\left(1-\Delta_{\ell,\ell'}\frac{\ell_c}{n_c}\right)J_{(\Delta_{n,n'}+1)}\left(\Delta_{n,n'}\epsilon\right)\right.\right. \\ &\left.\left.-\left(1+\Delta_{\ell,\ell'}\frac{\ell_c}{n_c}\right)J_{(\Delta_{n,n'}-1)}\left(\Delta_{n,n'}\epsilon\right)\right\}\right| \lesssim \frac{n^2}{2\left|\Delta_{n,n'}\right|} \ ,\end{aligned} \tag{30}$$

where $\Delta_{n,n'} = n - n'$ and $\Delta_{\ell,\ell'} = \ell - \ell'$. In Eq. (30) we also used: $n_c = 2nn'/(n+n')$, $\ell_c = \max(\ell,\ell')$ and finally $\epsilon^2 = 1 - \ell_c^2/n^2$. Clearly the last inequality of Eq. (30) is accurate only to the leading order in n, and to the same order it is equally correct if one uses either n or n' or n_c.

Finally, for $n\hat{p}_\imath\hat{r}_\jmath$ by using $\hat{p}_\imath = -i\left[\hat{r}_\imath, \hat{H}_0\right]$ and inserting a resolution of unity between the two operators one has:

$$\begin{aligned}&|n\ \langle n'\ell'm'|\hat{p}_\imath\hat{r}_\jmath|n''\ell''m''\rangle| \\ &\quad\approx \left|in\sum_\mu \frac{\Delta_{n',\mu}}{\mu {n'}^2}\langle n'\ell'm'|\hat{r}_\imath|\mu\rangle\langle\mu|\hat{r}_\jmath|n''\ell''m''\rangle\right| < \\ &\quad< |\langle n'\ell'm'|\hat{r}_\jmath|n''\ell''m''\rangle| \ ,\end{aligned} \tag{31}$$

where $\Delta_{n',\mu} = n' - n_\mu$, and where we used the final result of Eq. (30). In Eq. (31) for the sake of a simpler notation we adopted the following convention: $|\mu\rangle = |n_\mu\ell_\mu m_\mu\rangle$ (which we will often use in this section).

The result of Eq. (31) rests on the observation that in the semiclassical limit the radial matrix elements of $\hat{r}_\imath$ become rapidly very small for large Δ's, as one can easily see from Eq. (30); and one may safely assume that for nonnegligible matrix elements the difference between the two principal quantum numbers is always much smaller than any of the principal quantum numbers themselves (e.g. $\Delta_{n',\mu} \ll n', n_\mu$). Therefore one may legitimately neglect higher order corrections in $\Delta_{n',\mu}/n'$.

In fact, we assume precisely this important condition throughout our argument: that is, we assume that the variance of the distribution of the Rydberg wave packets over the hydrogenic principal quantum numbers is always much smaller than the principal quantum number at the center of the distribution, i.e., the approximate average principal quantum number of the Rydberg wave packet. This is a very realistic approximation for most laser pulses employed in the excitation of Rydberg electrons, and it breaks down only for ultrashort, ultralarge bandwidth pulses; or when the Rydberg state is excited in presence of ultrastrong external fields.

In what follows we conduct our analysis in the most general form. Although at some point we specialize our argument to the case $\hat{O} = \hat{r}_\imath$ which yields the largest off-diagonal contribution to the equations of motion, it will be easy to see that the treatment of the case $\hat{O} = n\hat{p}_\imath\hat{r}_\jmath$ is completely analogous.

Any off-diagonal matrix element of Eq. (26) can be written as:

$$\begin{aligned}\langle\psi_{n'}|e^{i\hat{H}t}\hat{O}e^{-i\hat{H}t}|\psi_n\rangle = \sum_{\ell',m'}\sum_{\ell,m}\bar{C}_{n'}(\ell',m')C_n(\ell,m) \\ \times\langle n'\ell'm'|e^{i\hat{H}t}\hat{O}e^{-i\hat{H}t}|n\ell m\rangle \ ,\end{aligned} \tag{32}$$

where we have expanded the states $|\psi_{n'}\rangle$ and $|\psi_n\rangle$, which are initially confined within the n'- and n-manifold respectively, as follows:

$$|\psi_n\rangle = \sum_{\ell,m} C_n(\ell,m)|n\ell m\rangle \ , \tag{33}$$

where the $C_n(\ell,m)$'s are some general coefficients, possibly complex.

As we mentioned before, these off-diagonal matrix elements are present in the equations of motion either when the high-energy electron is prepared in a wave packet, or when the electron is initially confined within a single n-manifold, in which case they represent the second order (in the external field) corrections to the dynamics.

The dynamics of the matrix elements of Eq. (32) is best studied in the interaction picture [72], and therefore it is convenient to set:

$$\begin{aligned}e^{-i\hat{H}t}|n\ell m\rangle &= \sum_\lambda \alpha_\lambda(t)e^{-iE_\lambda t}|\lambda\rangle \\ \langle n'\ell'm'|e^{+i\hat{H}t} &= \sum_\mu \beta_\mu(t)e^{+iE_\mu t}\langle\mu| \ ,\end{aligned} \tag{34}$$

where we used once again the convention $|\lambda\rangle = |n_\lambda\ell_\lambda m_\lambda\rangle$ and $|\mu\rangle = |n_\mu\ell_\mu m_\mu\rangle$, as the most important features of our argument depend on the spectrum of the hydrogen atom, and are determined solely by the principal quantum number of the state.

The equations of motion for the α's and the β's can be derived directly from the Schrödinger equation:

$$\begin{aligned}i\dot{\alpha}_\lambda &= F\sum_{\lambda_1}\langle\lambda|\hat{x}|\lambda_1\rangle\alpha_{\lambda_1}e^{-i(E_{\lambda_1}-E_\lambda)t} \\ i\dot{\beta}_\mu &= -F\sum_{\mu_1}\langle\mu_1|\hat{x}|\mu\rangle\beta_{\mu_1}e^{-i(E_\mu-E_{\mu_1})t} \ ,\end{aligned} \tag{35}$$

and the solution of Eqs. (35) to zeroth order in the field is:

$$\begin{aligned}\alpha^{(F^0)}_{n_\lambda\ell_\lambda m_\lambda} &= \delta_{n_\lambda,n}\delta_{\ell_\lambda,\ell}\delta_{m_\lambda,m} \\ \beta^{(F^0)}_{n_\mu\ell_\mu m_\mu} &= \delta_{n_\mu,n'}\delta_{\ell_\mu,l'}\delta_{m_\mu,m'} \ .\end{aligned} \tag{36}$$

In a first order approximation Eqs. (35) become:

$$\begin{aligned} i\dot{\alpha}_\lambda^{(F)} &= F\langle\lambda|\hat{x}|n\ell m\rangle e^{-i(E_n-E_\lambda)t} \\ i\dot{\beta}_\mu^{(F)} &= -F\langle n'\ell'm'|\hat{x}|\mu\rangle e^{+i(E_{n'}-E_\mu)t} \ , \end{aligned} \tag{37}$$

and their solution is straightforward:

$$\begin{cases} \alpha_\lambda^{(F)} = F\langle\lambda|\hat{x}|n\ell m\rangle \frac{e^{-i(E_n-E_\lambda)t}-1}{E_n-E_\lambda} & n_\lambda \neq n \\ \alpha_\lambda^{(F)} = -iF\langle\lambda|\hat{x}|n\ell m\rangle t & n_\lambda = n,\ \{\ell_\lambda, m_\lambda\} \neq \{\ell, m\} \\ \alpha_\lambda^{(F)} = 1 & \{n_\lambda, \ell_\lambda, m_\lambda\} = \{n, \ell, m\} \end{cases} \tag{38}$$

and also:

$$\begin{cases} \beta_\mu^{(F)} = F\langle n'\ell'm'|\hat{x}|\mu\rangle \frac{e^{+i(E_{n'}-E_\mu)t}-1}{E_{n'}-E_\mu} & n_\mu \neq n' \\ \beta_\mu^{(F)} = iF\langle n'\ell'm'|\hat{x}|\mu\rangle t & n_\mu = n',\ \{\ell_\mu, m_\mu\} \neq \{\ell', m'\} \\ \beta\mu^{(F)} = 1 & \{n_\mu, \ell_\mu, m_\mu\} = \{n', \ell', m'\} \end{cases} \tag{39}$$

Therefore, to first order in the external field the time dependence of the matrix elements of Eq. (32) is:

$$\begin{aligned} &\langle n'\ell'm'|e^{i\hat{H}t}\hat{O}e^{-i\hat{H}t}|n\ell m\rangle^{(F)} \\ &= F_1 \sum_{\substack{\lambda\neq n' \\ \lambda\neq n}} \langle n'\ell'm'|\hat{O}|\lambda\rangle\langle\lambda|\hat{x}|n\ell m\rangle \\ &\times \frac{e^{-i(E_n-E_{n'})t} - e^{-i(E_\lambda-E_{n'})t}}{E_n - E_\lambda} \\ &+ F_2 \sum_{\substack{\mu\neq n \\ \mu\neq n'}} \langle n'\ell'm'|\hat{x}|\mu\rangle\langle\mu|\hat{O}|n\ell m\rangle \\ &\times \frac{e^{-i(E_n-E_{n'})t} - e^{-i(E_n-E_\mu)t}}{E_{n'} - E_\mu} \\ &- iF_3 \sum_{\ell_\lambda, m_\lambda} \langle n'\ell'm'|\hat{O}|n\ell_\lambda m_\lambda\rangle\langle n\ell_\lambda m_\lambda|\hat{x}|n\ell m\rangle \\ &\times e^{-i(E_n-E_{n'})t} t \\ &+ F_4 \sum_{\ell_\lambda, m_\lambda} \langle n'\ell'm'|\hat{O}|n'\ell_\lambda m_\lambda\rangle\langle n'\ell_\lambda m_\lambda|\hat{x}|n\ell m\rangle \\ &\times \frac{e^{-i(E_n-E_{n'})t} - 1}{E_n - E_{n'}} \\ &+ iF_5 \sum_{\ell_\mu, m_\mu} \langle n'\ell'm'|\hat{x}|n'\ell_\mu m_\mu\rangle\langle n'\ell_\mu m_\mu|\hat{O}|n\ell m\rangle \\ &\times e^{-i(E_n-E_{n'})t} t \\ &+ F_6 \sum_{\ell_\mu, m_\mu} \langle n'\ell'm'|\hat{x}|n\ell_\mu m_\mu\rangle\langle n\ell_\mu m_\mu|\hat{O}|n\ell m\rangle \\ &\times \frac{e^{-i(E_n-E_{n'})t} - 1}{E_{n'} - E_n} \\ &+ \langle n'\ell'm'|\hat{O}|n\ell m\rangle e^{-i(E_n-E_{n'})t} \ , \end{aligned} \tag{40}$$

where we have attached subscripts to the field strength F only for bookkeeping purposes, and so $F_1 = F_2 = ... = F_6 = F$.

Clearly, all the terms of Eq. (40) oscillate with a frequency comparable (but not identical!) to the Kepler frequency ω_K of the hydrogenic manifold at the center of the distribution of principal quantum numbers. We indicate the principal quantum number of this special hydrogenic eigenmanifold as $\bar{n}$. For very weak external fields, the Kepler frequency is much larger than the Stark frequency of the motion. This is true for the classical conditions on the fields of Eq. (6) and also, albeit in a much stronger form, for the usual quantum condition of Eq. (9), i.e., the Inglis-Teller limit for negligible intermanifold mixing. This means that the wave packet oscillates several times before the classical perturbative equations of motion yield any significant change in the expectation values of angular momentum and Runge-Lenz vector. Therefore, following exactly the approach of *classical* perturbation theory for the derivation of Eqs. (4), we time average the quantum dynamics over the Kepler period $T_K = 2\pi\bar{n}^3$ of the $\bar{n}$-manifold approximately at the center of the energy distribution of the wave packet. Such time averaging does not affect the diagonal terms of Eq (26); however, it allows us to evaluate with accuracy the *secular*, off-diagonal contributions to the dynamics over a time $\tau = \gamma T_S$, that is, over some multiple of the Stark period T_S.

For a Rydberg electron confined within a n-manifold the Stark period T_S is defined as:

$$T_S = \frac{2}{3nF} \ . \tag{41}$$

However, its definition can be easily generalized to the case of a wave packet with average principal quantum number $\bar{n}$, by setting:

$$T_S \approx \frac{2}{3\bar{n}F} \ . \tag{42}$$

First, we consider the last term of Eq. (40) which is of zeroth order in the field; by inserting it in the perturbative equations of motion, i.e., in Eq. (26), one obtains an off-diagonal term which is of first order in the field. By first time averaging over a Kepler period, and then integrating over a time τ, and finally using Eq. (42 one obtains:

$$\begin{aligned} &\int_0^\tau F\langle n'|\hat{O}|n\rangle \left\langle e^{-i(E_n-E_{n'})t}\right\rangle_K d\tau' \\ &\qquad \approx \gamma\frac{2}{3\bar{n}}\langle n'|\hat{O}|n\rangle\frac{3}{\bar{n}}\left(\Delta_{\bar{n},n} - \frac{1}{2}\Delta_{n',n}\right) \ , \end{aligned} \tag{43}$$

where $\left\langle ... \right\rangle_K$ indicates the time averaging over the Kepler period, and where we used the following result (derived in Appendix B):

$$\begin{aligned} \left\langle e^{-i(E_n-E_{n'})t}\right\rangle_K &= \frac{1}{T_K}\int_0^{T_K} e^{\mp i(E_\imath - E_\jmath)t} dt \\ &= \frac{3}{\bar{n}}\left(\Delta_{\bar{n},\jmath} - \frac{1}{2}\Delta_{\imath,\jmath}\right) + O\left(\frac{\Delta^2}{\bar{n}^2}\right) \ . \end{aligned} \tag{44}$$

From Eq. (30) one has:

$$|\langle n'|\hat{O}|n\rangle| = |\langle n'|\hat{r}_\imath|n\rangle| \lesssim \frac{\bar{n}^2}{2|\Delta_{n',n}|} \ , \tag{45}$$

which holds only to the leading order in $\bar{n}$, and where a similar result can be obtained also in the case $\hat{O} = n\hat{p}_\imath \hat{r}_\jmath$ The final result is:

$$\begin{aligned} &\left| \int_0^\tau F \, \langle n'|\hat{O}|n\rangle \left\langle e^{-i(E_n - E_{n'})t} \right\rangle_K d\tau' \right| \\ &\lesssim \gamma \left| \frac{2\Delta_{\bar{n},n} - \Delta_{n',n}}{2|\Delta_{n',n}|} \right| \ll \bar{n} \, , \end{aligned} \tag{46}$$

where the last inequality follows under the very important assumption which we introduced before, i.e., that the variance of the distribution of the Rydberg wave packet over the principal quantum numbers is much smaller than the average principal quantum number of the wave packet. We conclude from Eq. (46) that first order, off-diagonal contributions are very small when compared to the dominating principal quantum number of the wave packet; indeed, this is a sufficient condition to neglect them completely, because the quantum expectation values of angular momentum and scaled Runge-Lenz vector range precisely from $-\bar{n}$ to $\bar{n}$. Most importantly, however, one must also require that $\gamma \sim 1$, i.e., the off-diagonal contribution remains small only up to times comparable to the Stark period; for longer times the secular effects build up and off-diagonal terms become relevant.

Clearly, the analysis above does not yet yield any information about the precise condition that the external field F must satisfy, so that all off-diagonal terms remain negligible. To learn more about it, one must analyze the off-diagonal contributions which are of second order in the field. We begin considering the terms of Eq. (40) which are proportional to F_1. By inserting any of them in the equations of motion for the expectation values of angular momentum and Runge-Lenz vector, one obtains contributions which are of second order in the external field; that is, to the leading order in $\bar{n}$ one obtains:

$$\begin{aligned} &\left| \int_0^\tau F^2 \langle n'\ell'm'|\hat{O}|\lambda\rangle\langle\lambda|\hat{x}|n\ell m\rangle \frac{\left\langle e^{-i(E_n - E_{n'})t} \right\rangle_K}{E_n - E_\lambda} d\tau' \right| \\ &\lesssim \gamma \left| \frac{\Delta_{\bar{n},\langle n\rangle}}{2\Delta_{n',\lambda}\Delta^2_{n,\lambda}} \right| F\bar{n}^5 \, , \end{aligned} \tag{47}$$

where $\langle n\rangle = (n+n')/2$, and we have used the results of Eqs. (42), (44) and (45); we have also used the following result (see Appendix B):

$$\begin{aligned} \frac{1}{E_\imath - E_\jmath} = \frac{\bar{n}^3}{\Delta_{\imath,\jmath}} \Bigg\{ 1 + \frac{3}{\bar{n}} \left(\Delta_{\jmath,\bar{n}} + \frac{1}{2}\Delta_{\imath,\jmath} \right) \\ + O\left(\frac{\Delta^2}{\bar{n}^2} \right) \Bigg\} \, . \end{aligned} \tag{48}$$

From Eq. (47) is finally possible to extract a necessary and sufficient condition on the field strength. By requiring that the result of Eq. (47) is much smaller than $\bar{n}$ one obtains:

$$F\bar{n}^4 \ll 1 \, , \tag{49}$$

which is essentially the same as the classical condition of Eq. (6), as we had claimed before.

Clearly, the same analysis applies to the terms of Eq. (40) which are proportional to F_2, and also to the oscillating part of the F_4 and F_6 terms.

Therefore, we next turn our attention to the remaining terms from Eq. (40), that is, the contributions which are proportional to F_3 and F_5 and also the non-oscillating parts of the F_4 and F_6 terms as well. First, one needs the time averages of the time dependent factors in the F_3 and F_5 sums, which are given by the following equation (see Appendix B):

$$\begin{aligned} &\left\langle it \, e^{-i(E_\imath - E_\jmath)t} \right\rangle_K = \frac{i}{T_K} \int_0^{T_K} t \, e^{-i(E_\imath - E_\jmath)t} dt \\ &= -\frac{\bar{n}^3}{\Delta_{\imath,\jmath}} \left\{ 1 - \frac{6}{\bar{n}} \left(\Delta_{\bar{n},\jmath} - \frac{1}{2}\Delta_{\imath,\jmath} \right) (1 + i\pi\Delta_{\imath,\jmath}) \right. \\ &\left. + O\left(\frac{\Delta^3}{\bar{n}^2} \right) \right\} \, . \end{aligned} \tag{50}$$

By inserting the time averaged F_3 and F_5 terms, along with the non oscillating parts of the F_4 and F_6 terms in the equations of motion and integrating over time one obtains (to the leading order in $\bar{n}$), an additional intermanifold correction, which we denote as $G(n'\ell'm'; n\ell m)$:

$$\begin{aligned} &G(n'\ell'm'; n\ell m) = \gamma T_S F \frac{\bar{n}^3}{\Delta_{n,n'}} \\ &\times \left\{ F_3 \sum_{\ell_\lambda, m_\lambda} \langle n'\ell'm'|\hat{O}|n\ell_\lambda m_\lambda\rangle\langle n\ell_\lambda m_\lambda|\hat{x}|n\ell m\rangle \right. \\ &- F_4 \sum_{\ell_\lambda, m_\lambda} \langle n'\ell'm'|\hat{O}|n'\ell_\lambda m_\lambda\rangle\langle n'\ell_\lambda m_\lambda|\hat{x}|n\ell m\rangle \\ &- F_5 \sum_{\ell_\mu, m_\mu} \langle n'\ell'm'|\hat{x}|n'\ell_\mu m_\mu\rangle\langle n'\ell_\mu m_\mu|\hat{O}|n\ell m\rangle \\ &\left. + F_6 \sum_{\ell_\mu, m_\mu} \langle n'\ell'm'|\hat{x}|n\ell_\mu m_\mu\rangle\langle n\ell_\mu m_\mu|\hat{O}|n\ell m\rangle \right\} \, . \end{aligned} \tag{51}$$

It is easy to see from the previous analysis of the F_1 terms that $G(n'\ell'm'; n\ell m)$ is a negligible intermanifold contribution if and only if the expression within the curly brackets of Eq. (50) scales as $\sim F\bar{n}^3$. However, each of the terms in the four sums consists of the product of two matrix elements, and our previous analysis of the magnitude of the matrix elements of $\hat{r}_\imath$ and also of any of the possible choices for $\hat{O}$, indicates that all such terms may scale as $\sim F\bar{n}^4$. Therefore, the desired scaling as the third power of $\bar{n}$ must originate from cross cancelations between the four sums within the curly brackets.

This is obviously correct when, for example, $\hat{O} = n\hat{L}_z$ and all the off-diagonal matrix elements of

$G(n'\ell'm';n\ell m)$ vanish, and one has:

$$\begin{aligned} &|G(n'\ell'm';n\ell m)| \\ &= \gamma\frac{2\bar{n}^2}{3|\Delta_{n,n'}|}|Fn\ (m-m')\langle n'\ell'm'|\hat{x}|n\ell m\rangle| \\ &\approx \gamma\frac{F\bar{n}^5}{3\Delta_{n,n'}^2} \end{aligned} \tag{52}$$

where we used Eq. (42), and also the usual selection rules to conclude that $m - m' = \pm 1$. A moment's thought shows that an essentially similar analysis holds also for the other components of the angular momentum.

The situation, instead, becomes much more complicated when $\hat{O} = \hat{r}_\imath$ or $\hat{O} = n\hat{p}_\imath\hat{r}_\jmath$ In those cases the pairing of terms which leads to the desired cross cancelations depends on the differences of the angular momentum quantum numbers; that is, it depends on $\Delta_{\ell',\ell}$ and possibly also on $\Delta_{m',m}$. For example, if $\ell = \ell' - 2$, by pairing an F_3 term with the corresponding F_4 term one obtains:

$$\begin{aligned} &\sum_{\ell_\lambda,m_\lambda}\eta\left(F_3R^{n,\ell_\lambda}_{n',\ell'}R^{n,\ell}_{n,\ell_\lambda} - F_4R^{n',\ell_\lambda}_{n',\ell'}R^{n,\ell}_{n',\ell_\lambda}\right) \\ &\approx \sum_{\ell_\lambda,m_\lambda}\eta FR^{n,\ell_\lambda}_{n',\ell'}\left(R^{n,\ell}_{n,\ell_\lambda} - R^{n',\ell_\lambda}_{n',\ell'}\right)\ , \end{aligned} \tag{53}$$

where η is a coefficient ~ 1 which contains the angular part of the matrix elements [82]. The difference of the two diagonal radial matrix elements scales as $\sim n \approx \bar{n}$, and therefore the whole expression scales as $\sim F\bar{n}^3$, which is the desired result. Note that in Eq. (53) one can approximately factor out an off-diagonal radial matrix element because both off-diagonal elements represent the same kind of transition, i.e., the principal quantum number *and* the angular momentum quantum number decrease in both cases (assuming that $n' > n$), that is the transitions are:

$$n' \to n\ ,\ \begin{cases}\ell' \to \ell_\lambda & \ell' > \ell_\lambda \\ \ell_\lambda \to \ell & \ell_\lambda > \ell\ .\end{cases} \tag{54}$$

Indeed, it is well known that the matrix element for an atomic transition which increases both the energy and the angular momentum of the electron is significantly larger than the one for a transition which brings about the same change in energy, but leads to a smaller final angular momentum [82]. Therefore, if $\Delta_{\ell',\ell} = 0$ a different, more complicated pairing of the terms must be employed, which in this case may depend also on the angular part of the matrix elements.

However, the scaling of $G(n'\ell'm';n\ell m)$ with the principal quantum number can most effectively and also more convincingly be studied by evaluating numerically the whole expression within the curly brackets of Eq. (51), divided by F. More precisely, for each pair $\{n', n\}$ we computed the maximum magnitude of the expression within curly brackets (divided by F) over all possible choices of angular quantum numbers, and we we denote it by $g(n', n)$, that is:

$$g(n',n) = \max_{\{\ell'm';\ell m\}}\left|\frac{\Delta_{n,n'}G(n'\ell'm';n\ell m)}{\gamma T_S F^2\bar{n}^3}\right|\ . \tag{55}$$

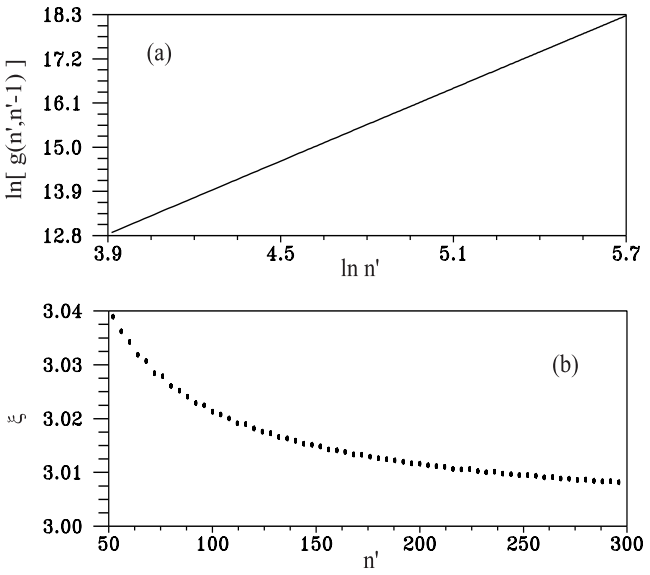

FIG. 1. Scaling of the intermanifold contribution with the principal quantum number. In Fig (a) we plot the natural logarithm of the maximum magnitude of the intermanifold terms vs. the natural logarithm of the principal quantum number, and the approximate straight line indicates a simple power-law scaling. In Fig (b) we plot the slope of the line in Fig. (a), i.e., the exponent of the power-law, which is clearly converging to $\xi = 3$, thereby proving that in the semiclassical limit all intermanifold contributions become negligible.

In Fig. 1-(a) we plot the logarithm of $g(n', n'-1)$ vs. the logarithm of n', setting $\hat{O} = \hat{x}$: this is the case in which $G(n'\ell'm';n\ell m)$ is the largest, as many numerical calculations confirm. The line in Fig. 1-(a) is almost exactly a straight, which confirms that $g(n', n'-1)$ scales with $n' \approx \bar{n}$ according to a power law, i.e. $g \sim \bar{n}^\xi$. However, the exponent ξ is not exactly constant, and in Fig. 1-(b) we plot the slope of the straight line of Fig. 1-(a) vs. n'. Clearly, for increasing n''s the exponent ξ is converging to 3, and that is precisely the result which we need to prove that $G(n'\ell'm';n\ell m)$ is truly a negligible intermanifold contribution to the equations of motion.

The proportionality coefficient of the power law can also be easily evaluated from the numerical data and one obtains:

$$g(n', n'-1) \approx 3.15{n'}^3 = 3.15\bar{n}^3\left\{1 + O\left(\frac{\Delta}{\bar{n}}\right)\right\}\ . \tag{56}$$

Finally, we have repeated the same calculations for several values of $\Delta_{n',n}$, and also for $\hat{O} = \hat{y}$, $\hat{z}$, and $\hat{O} = n\hat{p}_\imath\hat{r}_\jmath$, $\{\imath, \jmath\} = 1, 2, 3$. In all cases our findings were essentially identical to the ones of Fig. 1.

The physical interpretation of our result is particularly interesting. Rydberg wave packets which are relatively well localized in energy move along the trajectories of the classical electron or, for radial wave packets, of an ensemble of classical electrons [20–43]. However, unless some suitable external fields are applied to the system, [32–43], they do so only for a few Kepler periods. Such wave packets do not remain localized in the angular variable and therefore spread along the classical ellipse. Eventually they display interference fringes as the front of the packet catches up with its tail, and finally they also show quantum revivals and superrevivals [20–22, 25, 27–29]. However, from the point of view of the time averaged equations of motion the electron is *always* spread (i.e., averaged) along the classical trajectory, very much like in classical mechanics, where after time averaging the elements of the Kepler ellipse become the dynamical variables of the system, replacing the phase space coordinates of the electron. Therefore the time averaged, quantum equations of motion are insensitive to the spreading of the wave packet, and to its revivals, and that is why the same results as for stationary states can be legitimately extended to wave packets too.

Note that the results of our analysis can be generalized beyond the case of Rydberg electrons excited to wave packets, and hold also when the Rydberg electron is initially confined within a hydrogenic manifold, and n-mixing is brought about only by external field. In that case, in fact, one needs only to replace $\langle n'\ell'm'|$ with $\langle n\ell'm'|$. Clearly, for a Rydberg electron initially confined within a n manifold, all off-diagonal terms in the equations of motion for the quantum expectation values are of second order in the field, however they still derive from the first order terms of Eq. (40), and that is why the classical constraint on the external field of Eq. (49) holds in that case too.

Indeed, in the very important case of slow ion-Rydberg collisions the Rydberg electron is initially excited to a specific n-manifold, and in the next section we show that some special linear combinations of hydrogen atom eigenfunctions which are confined within a hydrogenic manifold (elliptic states [29, 67, 68]) yield the appropriate quasiclassical initial conditions for the quantum expectation values of angular momentum and Runge-Lenz vector, which then closely track the time averages of the classical variables.

IV. CLASSICAL, QUASICLASSICAL AND QUANTUM INITIAL CONDITIONS

In this section we discuss the initial conditions for the equations of motion for the quantum expectation values, and show that in the case of elliptic states [29, 67, 68] the quantum expectation values track exactly the time averages of the classical variables. More precisely, for a classical Kepler ellipse, initially in the xy-plane, and with the semimajor axis pointing along the x-axis, one has:

$$\begin{aligned} L_z &= n\sqrt{1-e^2}\ ,\ a_x = ne \\ L_x &= L_y = a_y = a_z = 0\ , \end{aligned} \tag{57}$$

where e is the eccentricity of the orbit, and, as usual, the energy of the classical electron is:

$$E = -\frac{1}{2n^2}\ . \tag{58}$$

On the other hand, for an elliptic state $|n\alpha\rangle$ (an elliptic state is given by a complicated superposition of spherical eigenstates of the hydrogen atom, all with the same principal quantum number [29, 67, 68]), which is also localized in the xy-plane, and oriented like the classical ellipse above, one has [29, 67, 68]:

$$\begin{aligned} &\langle n\alpha|\hat{L}_z|n\alpha\rangle = (n-1)\cos\alpha \\ &\langle n\alpha|\hat{a}_x|n\alpha\rangle = (n-1)\sin\alpha \\ &\langle n\alpha|\hat{L}_x|n\alpha\rangle = \langle n\alpha|\hat{L}_y|n\alpha\rangle = 0 \\ &\langle n\alpha|\hat{a}_y|n\alpha\rangle = \langle n\alpha|\hat{a}_z|n\alpha\rangle = 0\ , \end{aligned} \tag{59}$$

so that the correspondence between e and $\sin\alpha$ is established (obviously this α has no relation with the coefficients of the previous section). Clearly, in the limit of large n's the quantum expectation values and the classical predictions converge, and for elliptic states the quantum expectation values not only obey the same perturbative equations as the time averages of the classical variables, but also have almost the same initial conditions. Therefore they closely follow the same trajectories as the time averaged classical angular momentum and Runge-Lenz vector. This result has already been observed numerically [4, 51, 83], and also experimentally [4, 8] for some special configurations of the external fields. Most importantly, since elliptic states are coherent states of the angular momentum [29, 67, 68, 85], i.e., states of minimum uncertainty, it turns out that:

$$\begin{aligned} &\frac{\langle n\alpha|\hat{L}^2|n\alpha\rangle - \sum_\imath \langle n\alpha|\hat{L}_\imath|n\alpha\rangle^2}{\frac{1}{2}\left(\langle n\alpha|\hat{L}^2|n\alpha\rangle + \sum_\imath \langle n\alpha|\hat{L}_\imath|n\alpha\rangle^2\right)} \\ &= \frac{1}{(n-1)\cos^2\alpha + \frac{1}{2}}\ . \end{aligned} \tag{60}$$

and in the semiclassical limit the expectation values of $\hat{L}_\imath$, $\imath = 1, 2, 3$, are related to the expectation value of $\hat{L}^2$ approximately like in classical mechanics. In fact, it has been verified numerically in a few special cases [51, 83] that not only the expectation values of $\hat{L}_\imath$ and $\hat{a}_\imath$ evolve in time quasiclassically according to Eqs. (4), but also that during the time evolution the state remains elliptic. This is exactly the same situation as in classical mechanics, where the electron keeps moving along an ellipse, but the properties of the ellipse vary slowly in time; similarly, the numerical evidence shows that the elliptic state remains localized along a classical Kepler ellipse while it slowly evolves in time.

Instead, for the more familiar spherical eigenstates $|n\ell m\rangle$'s of the hydrogen atom the situation is completely different, and one has:

$$\begin{aligned} &\langle n\ell m|\hat{L}_z|n\ell m\rangle = m \\ &\langle n\ell m|\hat{L}_x|n\ell m\rangle = \langle n\ell m|\hat{L}_y|n\ell m\rangle = 0 \\ &\langle n\ell m|\hat{a}_x|n\ell m\rangle = \langle n\ell m|\hat{a}_y|n\ell m\rangle = \\ &= \langle n\ell m|\hat{a}_z|n\ell m\rangle = 0 \ , \end{aligned} \tag{61}$$

and the initial conditions differ dramatically from the classical ones, which leads to some interesting considerations.

As we explained before, the classical constraints of Eq. (7) remain invariant under the evolution of the perturbative equations. The second classical constraint translates into a condition over the quantum expectation values, which is also invariant:

$$\chi = \sum_\imath \left\{ \langle\psi|\hat{L}_\imath|\psi\rangle^2 + \langle\psi|\hat{a}_\imath|\psi\rangle^2 \right\} \ , \tag{62}$$

where $|\psi\rangle$ is any state (elliptic, spherical or also a wave packet, in which case the expectation value must also be averaged over a Kepler period) which satisfies the requirements of our derivation. The invariant χ is related to the Casimir operator of the SO(4) symmetry group of the hydrogen atom [76, 86]. The value of the classical invariant of Eq. (7) is n^2. For an elliptic state the quantum invariant of Eq. (62) is equal to $(n-1)^2$; however, for a spherical eigenstate χ is equal to m^2, which for the small m's typically excited by optical transitions from the initial low-n state to the Rydberg high-n state is a much smaller number than the classical result. This poses severe limits on the largest possible expectation value of any component of the angular momentum over a spherical eigenstate; this feature might be exploited in experiments to study the properties of Rydberg states.

The limitation which Eq. (62) imposes on the expectation values of angular momentum and Runge-Lenz vector over spherical eigenstates stems from the fact that such states have vanishing electric dipole moment; a small angular momentum is not balanced by a large Runge-Lenz vector, as it happens in classical ellipses and quantum elliptic states. More precisely, for spherical states, the electric field cannot induce first order dynamical effects because the expectation value of the Runge-Lenz vector over a spherical eigenstate is zero (i.e., there is no permanent electric dipole), and the state must first be distorted by the field so that the expectation value of the angular momentum (or Runge-Lenz vector) can change. This indicates that the dynamics must be at least of second order in the external fields. This situation is germane to the well known linear Stark effect [82], where degenerate perturbation theory and parabolic states must be used to account for the linear dependence of the eigenvalues on the external field. In fact, a spherical eigenstate can be seen as a superposition of elliptic states (or in a semiclassical interpretation an ensemble of Kepler ellipses), which are oriented uniformly in the xy-plane, so that the total Runge-Lenz vector is averaged to zero.

The (at least) quadratic dependence of the time evolution on the field can be explicitly verified by expanding the time dependent operators in the Heisenberg picture, [72] and by showing that the expectation values of the first order terms in the electric field vanish. Using the Hamiltonian of Eq. (2) (minus the diamagnetic term), and writing the hydrogen atom Hamiltonian as $\hat{H}_0$ one has:

$$\begin{aligned} e^{i\hat{H}t}\hat{L}_\imath e^{-i\hat{H}t} &= \hat{L}_\imath - it\left[\hat{H}_0 - \omega_L\hat{L}_z, \hat{L}_\imath\right] - itF\left[\hat{x}, \hat{L}_\imath\right] \\ &+ F\sum_p \frac{(-it)^p}{p!}\sum_{k=0}^{p-1}\Big[\hat{H}_0 - \omega_L\hat{L}_z, \Big[...\Big[x, \Big[\hat{H}_0 - \omega_L\hat{L}_z, [... \\ &... \Big[\hat{H}_0 - \omega_L\hat{L}_z, \hat{L}_\imath\Big] ...\Big]\Big]\Big]\Big] + O(F^2) \ , \end{aligned} \tag{63}$$

The simplest first order term is a direct commutator of the field with a component of the angular momentum: therefore it is either zero or a component of the position operator (depending on the index $\imath$), and its expectation value over a spherical eigenstate vanishes. Other, more complex first order terms come from the double sum in Eq. (63) and consist of a first series of k commutators of $\hat{L}_\imath$ with $\hat{H}_0 - \omega_L\hat{L}_z$, and then of a commutator with the field, and finally of a second series of $(p-1-k)$ commutators with $\hat{H}_0 - \omega_L\hat{L}_z$. It is easy to see that the expectation value of any of such terms over a spherical eigenstate of the hydrogen atom which is quantized along the z-axis vanishes, simply because such state is an eigenstates of $\hat{H}_0 - \omega_L\hat{L}_z$. However, the same result can be proven as follows also when the atom is quantized along an arbitrary direction. I) The first series of k commutators either vanishes or yields a component of the angular momentum (depending on the index $\imath$); II) the commutator of the result of step I with the electric field either vanishes or yields a component of the position operator; III) finally, the result of steps I and II must be commuted $(p-1-k)$ times with with $\hat{H}_0 - \omega_L\hat{L}_z$; this sequence of commutators can be organized so that one does first the commutators with $\hat{L}_z$ and next those with $\hat{H}_0$ because these two operators commute with one another. Obviously, the expectation value of the commutator of any operator with $\hat{H}_0$ vanishes, if it is taken over an eigenstate of $\hat{H}_0$ itself. On the other hand the commutators with $\hat{L}_z$ either vanish directly or yield a component of the position operator, whose expectation value over a spherical state also vanishes, and our point is proved.

Similar considerations apply also to $\hat{L}^2$. In fact, it is even easier to demonstrate that the time evolution of the expectation value of $\hat{L}^2$ over a spherical eigenstate of the hydrogen atom is of second order in the field. Clearly, $|n\ell m\rangle$ is an eigenstate of $\hat{L}^2$ and the expectation value of the commutator of $\hat{x}$ with $\hat{L}^2$ over $|n\ell m\rangle$ vanishes. Moreover, $\hat{L}^2$ commutes with $\hat{H}_0 - \omega_L\hat{L}_z$ and therefore the sequence of commutators similar the one of Eq. (63)

can be rearranged so that first one commutes the field operator with $\hat{H}_0 - \omega_L \hat{L}_z$, and next the result is commuted with $\hat{L}^2$. However, the expectation value over $|n\ell m\rangle$ of the commutator of any operator with $\hat{L}^2$ vanishes, which proves our point. Clearly, this result does not depend on the orientation of the axis of quantization of the atom relative to the external fields.

Note that even if the time evolution of the expectation values of $\hat{L}_\imath$ and $\hat{L}^2$ is only of second order in the external field, that does not imply that weak external fields are not effective in bringing about changes of the angular momentum. For example, in the expansion of Eq. (63) the second order terms are multiplied by at least a square power of the time; if we consider times comparable to the Stark period and the scaling of the matrix elements of the position operator with the principal quantum number as given in Eq. (28), it is easy to see that the final result is not negligible. Moreover, the constraint on the quantum invariant χ of Eq. (62) does not say much about the total angular momentum of a spherical state, which is not a coherent state of the angular momentum, and therefore not only one has:

$$\sum_\imath \langle n\ell m|\hat{L}_\imath|n\ell m\rangle^2 \neq \langle n\ell m|\hat{L}^2|n\ell m\rangle \qquad (64)$$

but the difference between the two sides of the equation can be very large, as one can see by considering a state with $\ell = n-1$ and $m = 0$.

Since the results of the previous section show that under the classical conditions for the external fields intermanifold contributions to the dynamics can be neglected, all our considerations apply also to a superposition of spherical states with different n's, and therefore our analysis sheds some light on the nature of the Rydberg states employed in ZEKE spectroscopy.

In ZEKE, ultrahigh molecular Rydberg states [5–7, 52–55] are first excited by a few optical transitions and successively field ionized. This technique is extremely successful because of the ultralong lifetimes of these Rydberg states, which are explained in terms of extensive intrashell mixing of the initial, unstable low-ℓ states with the longer lived high-ℓ states. For increasing angular momenta the coupling between the Rydberg electron and the molecular core becomes rapidly negligible, so that autoionization and predissociation channels are effectively quenched, and the Rydberg state becomes ultralong-lived. Therefore it is understood that ZEKE states, i.e., the ultralong-living Rydberg states responsible for the ZEKE signal, are complicated superpositions of large-n spherical eigenstates of the hydrogen atom, which are skewed in favor of large angular momentum states. Because of the small spacing of high-n Rydberg eigenenergies and of the width of the initial laser pulses, ZEKE states initially consist of a superposition of several states with different principal quantum numbers [56, 57]. However, it is generally assumed that only one angular momentum quantum number is allowed in the superposition because of the usual selection rules. The population of higher-ℓ states is ascribed solely to the effect of external fields.

In fact, several experimental studies [5–7, 58] have shown that the vanishingly small stray fields of the experimental set-up and, most importantly, the very weak, slowly varying electric fields of the ions present in the interaction region populate with great efficacy the high-ℓ Rydberg states which are responsible for the observed ultralong lifetimes of ZEKE states. On the theoretical side recent results [47–50, 56, 57], some of which were based on the classical perturbative approach of Eqs. (4) [47–50], have explained ℓ-mixing in terms of the hydrogenic model, in which vanishingly small fields are sufficient to induce the desired scrambling of the angular momentum quantum numbers. The great effectiveness with which such extremely weak fields ($F \lesssim 1V/m$) populate high-ℓ states strongly suggests that the hydrogenic model is indeed appropriate to describe angular momentum mixing in ZEKE states. Moreover, our present findings show that the previous classical results [47–50] are really quantum mechanical in nature, and can also be extended to the case of wave packets. On the other hand, the low-ℓ states excited by the laser pulse have a nonnegligible quantum defect, which decouples them from the high-ℓ, quasi-hydrogenic states; it is then likely that another mechanism is at work. More precisely, it is possible that the initial optical excitation of the ultrahigh-n states may not be strictly limited by the standard selection rules. Instead, by contributions which are of higher order in the optical field and yet are nonnegligible because of the ultralarge dipole moments of Rydberg states -see Eq. (28) and Eq. (29)-, the initial optical pulse may well populate a few angular momentum states with relatively large ℓ's, as one of us has recently shown [87]. Therefore, some degree of angular momentum mixing is probably already present in the initial Rydberg state, in which case the hydrogenic model, in its present extension to superpositions of states with different quantum numbers, provides an accurate description of how weak stray and ionic fields bring about the (approximate) randomization in ℓ and m of ZEKE states, which accounts for the observed ultralong lifetimes.

Finally, the extension of equations Eq. (4) from purely classical variables to quantum expectation values lends strength to a previous argument of ours concerning slow, ion-Rydberg collisions and which until now was based solely on purely classical calculations [47, 48]. More precisely, we suggested the need for a review of both experimental and theoretical results for the intrashell transitions induced in Rydberg alkali atoms by slow collisions with ions. In the case of slow ion-Rydberg collisions the "magnetic" term of the Hamiltonian arises from the rotation frequency of the field, and the problem is treated in the frame rotating with the field itself. In that frame the Hamiltonian is equivalent to the one of a hydrogenic electron in weak electric and magnetic fields of constant orientation, and time dependent magnitude [17, 47–49].

The ratio of the two magnitudes, however, remains constant, and Eq. (4) can be solved exactly [47–49]. It is then easy to see that after a full collision, the expectation value of $\hat{L}_z$ is over a spherical eigenstate (that is with the initial conditions of Eq. (61)), is [47, 48]:

$$\lim_{t\to\infty} \langle n\ell m|\hat{L}_z(t)|n\ell m\rangle = \frac{4b^2\tilde{v} - 9n^2}{4b^2\tilde{v} + 9n^2} m \qquad (65)$$

where b is the impact parameter of the collision, and $\tilde{v}$ is the "reduced" velocity of the incoming ion, *i.e.* its velocity in atomic units multiplied by n, which is the principal quantum number of the Rydberg electron in the target. In a first approximation, one may insert in Eq. (65) an average impact parameter $b \sim 50n^2$ and a reduced velocity $\tilde{v} \sim 1$, which are consistent with the experimental conditions, and the coefficient multiplying m becomes $\gtrsim 0.9$. Therefore the expectation value of $\hat{L}_z$ cannot change much, and if initially the electron is prepared in a $m \neq 0$ state, the expectation value of $\hat{L}_z$ will not vanish. However, both in the interpretation of the experimental data [62], and also in fully quantum theoretical treatments [63, 88–90] the assumption has been made of a uniform population of the m substates, which corresponds to a zero expectation value of $\hat{L}_z$. For high ℓ states this is a reasonably good approximation, even in the case of a non vanishing expectation value of $\hat{L}_z$. However the approximation clearly breaks down for smaller values of ℓ, which is precisely the regime for which we suggested a critical review of current results.

V. CONCLUSIONS

In this paper we have shown that under realistic conditions, the classical and quantum dynamics of Rydberg electrons in weak, slowly varying external fields agree beyond the mandates of Ehrenfest theorem.

We have shown that for the hydrogen atom in weak, slowly varying electric and magnetic fields, to first order in the applied fields the quantum expectation values of the components of the angular momentum and the Runge-Lenz vector obey exactly the same equations as the time averages (over a Kepler period and along a Kepler ellipse) of the corresponding classical variables. Our proof follows in spirit the approach of classical perturbation theory, as we fully exploit the properties of the zeroth order solutions of the quantum problem, exactly as one does in classical mechanics where the time averaging is done along Kepler ellipses, i.e., the zeroth order solutions of the classical problem. Note that this result is not an application of Ehrenfest's theorem, because the perturbative approach does not consist of the linearization of the problem in the neighborhood of an equilibrium point. Instead, it is an extension, in stronger form, of the theorem for the important case of the hydrogen atom in weak external fields.

Most importantly, in our derivation we have not applied Pauli's replacement directly in the Hamiltonian [31, 51, 83], and therefore we have been able to investigate the intermanifold contributions to the dynamics. In fact, by time averaging the dynamics over a Kepler period (which, again, is exactly the same procedure as in classical perturbation theory) we have shown that intermanifold terms do not contribute significantly to the evolution of the quantum expectation values, as long as the strength of the external fields satisfies the same requirement as in classical mechanics. Interestingly, in the semiclassical limit the classical constraint is much weaker than the quantum condition for negligible n-mixing, i.e., the Inglis-Teller limit.

This paradox can be resolved by observing that the perturbative equations remain accurate only up to times comparable to the Stark period, that is, for times which in atomic units are $\sim 1/\Delta E$, where ΔE is the energy separation between two Stark levels. Therefore, over such relatively short times the stationary picture of the Stark eigenstates which spread out of a hydrogenic n-manifold does not have much physical significance, and that is why for these relatively short times the more stringent quantum condition can be ignored.

Moreover, by time averaging the intermanifold dynamics we have also extended the validity of the classical perturbative equations to the case of Rydberg wave packets, as long as the spread of the packet over the hydrogenic eigenmanifolds is small compared to its average principal quantum number. Note, however, that although our analysis shows that the quantum expectation values of angular momentum and Runge-Lenz vector evolve in time like the classical time averaged variables, *it says nothing about the localization of the wave packet and the quasiclassical dynamics of the packet itself.* In fact, our time averaging is precisely equivalent to considering a spread out version of the wave packet, smeared along its orbit. This is the same situation as in classical mechanics, where one studies the motion of the Kepler ellipse, as if it the classical electron had been magically smeared along its own trajectory.

We have also demonstrated that the close quantum-classical equivalence can be extended, in the limit of very large principal quantum numbers, to the initial conditions of the equations of motion, provided that the expectation values are taken over elliptic states, which are states localized along the classical solutions [29, 67, 68]. Therefore the quantum expectation values of angular momentum and Runge-Lenz vector over elliptic states follow essentially the same trajectories as the time averages of the corresponding classical variables. Such complete quantum-classical equivalence, however, does not hold for the more familiar spherical eigenstates ($|n\ell m\rangle$) of the hydrogen atom.

The realization that the hydrogenic, perturbative equations of motion (which account so well for several physical phenomena) can also be interpreted as purely quantum mechanical equations has led to some insight

into the nature the Rydberg states employed in ZEKE spectroscopy; it also lends support to our result (previously only classical) which indicates that the averaging over the $\hat{L}_z$ sublevels (which is used in quantum close-coupling calculations to the end of making the problem of ion-Rydberg collisions numerically more tractable, and also in the interpretation of experimental data) may be unjustified.

Finally, one may wonder if the special equivalence between the dynamics of the time averages of classical variables and quantum expectation values is a peculiarity of the hydrogen atom in weak external fields, or if it can be extended to other weakly perturbed integrable systems, and the investigation of this problem is in progress in our groups.

APPENDIX A: PROOF OF THE IDENTITY OF EQ. (10)

In our proof of the special quantum-classical equivalence of the dynamics of Rydberg electrons in weak external fields, we have made extensive use of the following identity:

$$\langle\psi_n|\hat{r}_\imath\hat{p}_\jmath|\psi_n\rangle = -\langle\psi_n|\hat{p}_\imath\hat{r}_\jmath|\psi_n\rangle \ , \tag{A1}$$

where $\hat{r}_\imath$ and $\hat{p}_\jmath$ are components of the position and momentum operator respectively, and where $|\psi_n\rangle$ is a state confined within a hydrogenic n-manifold.

In this appendix we prove explicitly the identity of Eq. (A1), and we do so for all the pairs of indexes $\{\imath,\jmath\}$ to stress that our derivation of the equations of motion does not depend on the relative orientation between the initial axis of quantization of the atom and the direction of the applied, external fields in the Hamiltonian of Eq. (2).

We begin with the simplest case, that is when $\imath=\jmath$:

$$\begin{aligned}&\langle\psi_n|\hat{x}_\imath\hat{p}_\imath+\hat{p}_\imath\hat{x}_\imath|\psi_n\rangle\\ &\qquad=-i\langle\psi_n|\hat{x}_\imath\left[\hat{x}_\imath,\hat{H}_0\right]+\left[\hat{x}_\imath,\hat{H}_0\right]\hat{x}_\imath|\psi_n\rangle\\ &\qquad=-i\langle\psi_n|\left[\hat{x}_\imath^2,\hat{H}_0\right]|\psi_n\rangle=0\ ,\end{aligned} \tag{A2}$$

where $\hat{H}_0$ is the hydrogen atom Hamiltonian and the result follows because $|\psi_n\rangle$ is an eigenstate of $\hat{H}_0$. The same approach could be easily extended to all cases. However, for the cases in which $\imath\neq\jmath$ a different approach is more convenient to the end of studying the intermanifold contributions to the equations of motion, which we do in the main text of the paper [see Eq. (27)]. Indeed, a different proof identifies explicitly the nonclassical terms of the Heisenberg equations of motion; these are operators which have no counterpart in the classical equations. Such terms (see below) yield a null expectation value over states which are confined within an n-manifold, and also negligible intermanifold contributions to the equations of motion (see main text).

Therefore, we consider next the case $\imath=2$, $\jmath=1$:

$$\begin{aligned}\hat{y}\hat{p}_x&=-i\hat{y}\left[\hat{p}_y,\hat{L}_z\right]\\ &=-i\hat{y}\hat{p}_y\hat{L}_z+i\left\{\left[\hat{y},\hat{L}_z\right]\hat{p}_y+\hat{L}_z\hat{y}\hat{p}_y\right\}\\ &=-\hat{x}\hat{p}_y+i\left\{\hat{L}_z\hat{y}\hat{p}_y-\hat{y}\hat{p}_y\hat{L}_z\right\}\ .\end{aligned} \tag{A3}$$

We must then show that the expectation value over $|\psi_n\rangle$ of the operator within curly brackets vanishes, that is:

$$\langle\psi_n|\hat{L}_z\hat{y}\hat{p}_y-\hat{y}\hat{p}_y\hat{L}_z|\psi_n\rangle=0\ . \tag{A4}$$

Clearly, the state $|\psi_n\rangle$ can be written as:

$$|\psi_n\rangle=\sum_{\ell,m}C_n(\ell,m)|n\ell m\rangle\ , \tag{A5}$$

where the $C_n(\ell,m)$'s are some general coefficients, possibly complex. By substituting the expansion of Eq. (A5) in the expectation value of Eq. (A4) one has:

$$\begin{aligned}&\langle\psi_n|\hat{L}_z\hat{y}\hat{p}_y-\hat{y}\hat{p}_y\hat{L}_z|\psi_n\rangle\\ &=\sum_{\ell',m'}\sum_{\ell,m}\bar{C}_n(\ell',m')C_n(\ell,m)\Big\{m'\langle n\ell'm'|\hat{y}\hat{p}_y|n\ell m\rangle\\ &-m\langle n\ell'm'|\hat{y}\hat{p}_y|n\ell m\rangle\Big\}\ ,\end{aligned} \tag{A6}$$

where $\bar{C}_n(\ell',m')$ denotes the complex conjugate. On the other hand, from Eq. (A2) it follows that:

$$\begin{aligned}&\langle n\ell'm'|\hat{y}\hat{p}_y+\hat{p}_y\hat{y}|n\ell m\rangle\\ &\qquad=\langle n\ell'm'|2\hat{y}\hat{p}_y+[\hat{p}_y,\hat{y}]\,|n\ell m\rangle=0\ ,\end{aligned} \tag{A7}$$

and therefore the matrix elements of $\hat{y}\hat{p}_y$ are:

$$\langle n\ell'm'|\hat{y}\hat{p}_y|n\ell m\rangle=\frac{i}{2}\delta_{\ell'\ell}\delta_{m'm}\ . \tag{A8}$$

By inserting the matrix elements of Eq. (A8) in the double sum of Eq. (A6) it is easy to see that each term within curly brackets vanishes exactly, and therefore the identity of Eq. (A4) is proved.

Next, we consider the case $\imath=3$, $\jmath=1$. One has:

$$\begin{aligned}\hat{z}\hat{p}_x&=i\hat{z}\left[\hat{p}_z,\hat{L}_y\right]\\ &=i\hat{z}\hat{p}_z\hat{L}_y-i\left\{\left[\hat{z},\hat{L}_y\right]\hat{p}_z+\hat{L}_y\hat{z}\hat{p}_z\right\}\\ &=-\hat{x}\hat{p}_z-i\left\{\hat{L}_y\hat{z}\hat{p}_z-\hat{z}\hat{p}_z\hat{L}_y\right\}\ ,\end{aligned} \tag{A9}$$

and so we must prove that:

$$\langle\psi_n|\hat{L}_y\hat{z}\hat{p}_z-\hat{z}\hat{p}_z\hat{L}_y|\psi_n\rangle=0\ . \tag{A10}$$

We use:

$$\hat{L}_y=\frac{1}{2i}\left(\hat{L}_+-\hat{L}_-\right)\ , \tag{A11}$$

and also:

$$\hat{L}_+|n\ell m\rangle = \sqrt{(\ell-m)(\ell+m+1)}|n\ell m+1\rangle$$
$$\hat{L}_-|n\ell m\rangle = \sqrt{(\ell+m)(\ell-m+1)}|n\ell m-1\rangle\ , \quad \text{(A12)}$$

and the expectation value of Eq (A10) becomes:

$$\begin{aligned}
&\langle\psi_n|\hat{L}_y\hat{z}\hat{p}_z - \hat{z}\hat{p}_z\hat{L}_y|\psi_n\rangle \\
&= \frac{1}{2i}\sum_{\ell',m'}\sum_{\ell,m}\bar{C}_n(\ell',m')C_n(\ell,m) \\
&\times\Big\{\sqrt{(\ell'+m')(\ell'-m'+1)}\langle n\ell'm'-1|\hat{z}\hat{p}_z|n\ell m\rangle \\
&-\sqrt{(\ell'-m')(\ell'+m'+1)}\langle n\ell'm'+1|\hat{z}\hat{p}_z|n\ell m\rangle \\
&-\sqrt{(\ell-m)(\ell+m+1)}\langle n\ell'm'|\hat{z}\hat{p}_z|n\ell m+1\rangle \\
&+\sqrt{(\ell+m)(\ell-m+1)}\langle n\ell'm'|\hat{z}\hat{p}_z|n\ell m-1\rangle\Big\}\ .
\end{aligned} \quad \text{(A13)}$$

Clearly, the matrix elements of $\hat{z}\hat{p}_z$ are also given by Eq. (A8), and by inserting that result in Eq. (A13) it is easy to verify that once again the expression within curly brackets vanishes.

Finally, an essentially similar argument proves that the identity of Eq. (11) holds also for $\hat{z}\hat{p}_y$, which completes our proof.

APPENDIX B: TIME AVERAGING OF THE INTERMANIFOLD DYNAMICS

In this appendix we evaluate explicitly the time averages over a Kepler period T_K of the intermanifold contributions to the equations of motion for the quantum expectation values.

We begin with:

$$\left\langle e^{\mp i(E_\imath - E_\jmath)t}\right\rangle_K = \frac{1}{T_K}\int_0^{T_K} e^{\mp i(E_\imath-E_\jmath)t}dt \quad \text{(B1)}$$

The integral of Eq. (B1) is easily evaluated, and one has:

$$\frac{1}{T_K}\int_0^{T_K} e^{\mp i(E_\imath-E_\jmath)t}dt = \pm i\frac{e^{\mp i(E_\imath-E_\jmath)T_K}-1}{(E_\imath-E_\jmath)T_K} \quad \text{(B2)}$$

However, the energy difference $E_\imath - E_\jmath$ is:

$$\begin{aligned}
E_\imath - E_\jmath &= -\left(\frac{1}{2\imath^2}-\frac{1}{2\jmath^2}\right) \\
&= \frac{\Delta_{\imath,\jmath}}{\jmath^3} - \frac{3\Delta_{\imath,\jmath}^2}{2\jmath}\frac{1}{\jmath^3} + O\left(\frac{\Delta_{\imath,\jmath}^3}{\jmath^5}\right)\ ,
\end{aligned} \quad \text{(B3)}$$

where $\Delta_{\imath,\jmath} = \imath - \jmath$. We then use:

$$\jmath = \bar{n}\left(1+\frac{\Delta_{\jmath,\bar{n}}}{\bar{n}}\right)\ , \quad \text{(B4)}$$

where $\Delta_{\jmath,\bar{n}} = \jmath - \bar{n}$ and $\bar{n}$ is the principal quantum number of the hydrogenic manifold which carries the largest weight in the state. The energy difference between two manifolds can then be rewritten as:

$$E_\imath - E_\jmath = \frac{\Delta_{\imath,\jmath}}{\bar{n}^3}\left\{1-\frac{3}{\bar{n}}\left(\Delta_{\jmath,\bar{n}}-\frac{1}{2}\Delta_{\imath,\jmath}\right)\right\} + O\left(\frac{\Delta^3}{\bar{n}^5}\right). \quad \text{(B5)}$$

where Δ^3 (i.e., with no indexes) stands for the product of any three Δ's regardless of the indices. The Kepler period is:

$$T_K = 2\pi\bar{n}^3 \quad \text{(B6)}$$

Substituting the results of Eq. (B5) and Eq. (B6) in Eq. (B2) one obtains:

$$\begin{aligned}
&\frac{1}{T_K}\int_0^{T_K} e^{\mp i(E_\imath-E_\jmath)t}dt \\
&= \frac{3}{\bar{n}}\left(\Delta_{\bar{n},\jmath}-\frac{1}{2}\Delta_{\imath,\jmath}\right) + O\left(\frac{\Delta^2}{\bar{n}^2}\right)\ .
\end{aligned} \quad \text{(B7)}$$

Note that to the leading order in $\Delta/\bar{n}$ the result does not depend on the sign of the exponent; in fact, the leading term of the right hand side of Eq. (B7) can be cast in a more symmetric form:

$$\Delta_{\bar{n},\jmath} - \frac{1}{2}\Delta_{\imath,\jmath} = \Delta_{\bar{n},\imath} - \frac{1}{2}\Delta_{\jmath,\imath} = \bar{n} - \frac{1}{2}(\imath+\jmath) \quad \text{(B8)}$$

which concludes the calculation of the first time average.

Incidentally, by inverting to the leading order the expression of Eq. (B5) we obtain a result which we used in the main text of this paper:

$$\frac{1}{E_\imath - E_\jmath} = \frac{\bar{n}^3}{\Delta_{\imath,\jmath}}\left\{1+\frac{3}{\bar{n}}\left(\Delta_{\jmath,\bar{n}}-\frac{1}{2}\Delta_{\imath,\jmath}\right)\right\} + O\left(\frac{\Delta^3}{\bar{n}^5}\right). \quad \text{(B9)}$$

Next we evaluate:

$$\left\langle it\ e^{-i(E_\imath-E_\jmath)t}\right\rangle_K = \frac{i}{T_K}\int_0^{T_K} t\ e^{-i(E_\imath-E_\jmath)t}dt \quad \text{(B10)}$$

Once again, the integral is straightforward:

$$\begin{aligned}
&\frac{i}{T_K}\int_0^{T_K} t\ e^{-i(E_\imath-E_\jmath)t}dt = \frac{1}{(E_\imath-E_\jmath)T_K} \\
&\times\left\{i\frac{e^{-i(E_\imath-E_\jmath)T_K}-1}{(E_\imath-E_\jmath)} - T_K e^{-i(E_\imath-E_\jmath)T_K}\right\}\ .
\end{aligned} \quad \text{(B11)}$$

Finally, inserting in Eq. (B11) the results of Eqs. (B3-B6) one obtains:

$$\begin{aligned}
&\frac{i}{T_K}\int_0^{T_K} t\ e^{-i(E_\imath-E_\jmath)t}dt = -\frac{\bar{n}^3}{\Delta_{\imath,\jmath}}\Big\{1 \\
&-\frac{6}{\bar{n}}\left(\Delta_{\bar{n},\jmath}-\frac{1}{2}\Delta_{\imath,\jmath}\right)(1+i\pi\Delta_{\imath,\jmath}) + O\left(\frac{\Delta^3}{\bar{n}^2}\right)\Big\}\ ,
\end{aligned} \quad \text{(B12)}$$

which concludes our analysis.

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